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(54) **METHOD OF MANUFACTURING
NON-FIRING TYPE ELECTRODE**

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See application file for complete search history.

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(57) **ABSTRACT**

A method of manufacturing a non-firing type electrode com-
prising steps of: (A) applying a conductive paste on a sub-
strate; (B) heating the applied conductive paste at 50 to 350°
C. to form an electrode; and (C) pressing the electrode at 10 to
1000 kN/m² of plane surface pressure or at 5 to 300 kN/m of
linear pressure.

10 Claims, 1 Drawing Sheet

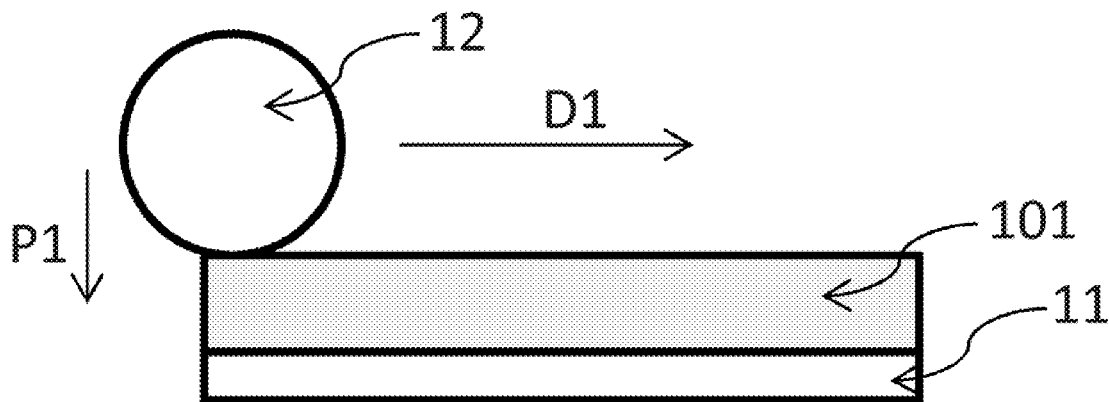


FIG. 1A



FIG. 1B

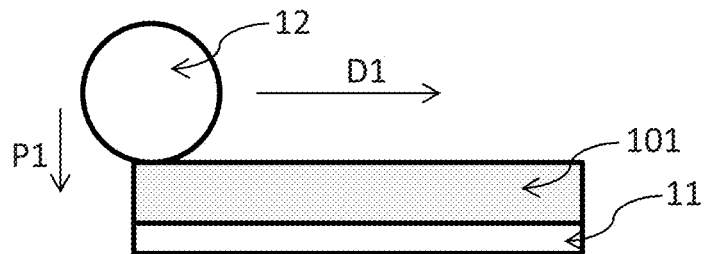


FIG. 1C

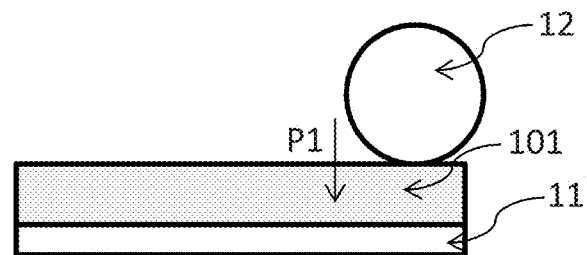
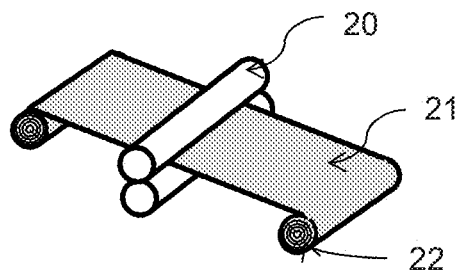


FIG. 2



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METHOD OF MANUFACTURING NON-FIRING TYPE ELECTRODE

FIELD OF INVENTION

The present invention relates to a method of manufacturing a non-firing type electrode.

TECHNICAL BACKGROUND OF THE INVENTION

Non-firing type electrodes are widely used in various electrical devices. The term "non-firing type electrode" is defined as an electrode formed without a heat treatment at temperature of 350° C. or higher.

US20090169724 discloses a method for producing a non-firing type electrode of membrane touch switch by (a) screen printing a conductive paste containing silver powder, phenoxo resin, urethane resin and an organic solvent on a polymer film, and (b) heating the printed conductive paste at 140° C.

BRIEF SUMMARY OF THE INVENTION

An objective is to provide a method of manufacturing a non-firing type electrode which can have sufficient electrical property.

An aspect of the invention relates to a method of manufacturing a non-firing type electrode comprising steps of: (A) applying a conductive paste on a substrate; (B) heating the applied conductive paste at 50 to 350° C. to form an electrode; and (C) pressing the electrode at 10 to 1000 kN/m² of plane surface pressure or at 5 to 300 kN/m of linear pressure.

Another aspect of the invention relates to an electrical device comprising the non-firing type electrode manufactured by the method above.

The non-firing type electrode having sufficient conductivity can be formed by the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1, A to C, explains an embodiment of the method of manufacturing the electrode in the present invention.

FIG. 2 illustrates an embodiment of roll to roll system in the step of pressing the electrode by a calendar roll.

DETAILED DESCRIPTION OF THE INVENTION

The method of manufacturing the non-firing type electrode comprises steps of (A) applying on a substrate a conductive paste, (B) heating the applied conductive paste to form an electrode, and (C) pressing the electrode. The method and materials to form non-firing type electrode explained below. Method of Manufacturing an Electrode

An example of the method of manufacturing the non-firing type electrode is explained with reference to FIG. 1A to 1C.

The conductive paste **10** is applied onto a substrate **11** as illustrated in FIG. 1A. To apply the conductive paste on the substrate, screen printing, stencil printing, gravure printing, offset printing, spin coating, blade coating, casting, or nozzle discharge can be available. The screen printing can be selected because the paste can be quickly screen printed in the desired pattern on a substrate in an embodiment.

The substrate **11** can be glass substrate, polymer film, semiconductor substrate, ceramic substrate or metal substrate in an embodiment. The substrate **11** can be selected depending on electrical devices, for example a glass or polymer

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substrate for a touch panel, a semiconductor substrate for a solar cell, and a ceramic substrate for a capacitor or a chip resistor. A metal substrate that has good thermal conductivity can be suitable for an electrical device that needs heat radiation such as a light emitter diode (LED). When the substrate **11** is a metal substrate or a semiconductor substrate, an insulating layer can be formed on the substrate **11** to not get electrical continuity between the substrate and the formed electrode.

In an embodiment, the substrate **11** can be a polymer film. The polymer film is flexible enough to not be broken by pressing. The polymer film can be a polyethylene terephthalate (PET) film, polyethylene naphthalate (PEN) film, polyimide (PI) film, polyimideamide film, polyamide film, polypropylene film, or polyethylene film. In the event of heating the conductive paste at over 100° C. in the later heating step, the polymer substrate can be the polymer film having heat resistance such as the PET film, PEN film or the PI film.

The applied conductive paste **10** on the substrate **11** is heated. By heating, the applied conductive paste which is viscous can be non-viscous enough to not be adhesive to a pressing tool in the subsequent pressing step. The heating temperature is 50 to 350° C., 60 to 250° C. in another embodiment, 70 to 200° C. in another embodiment. The heating time can be 1 to 120 minutes in an embodiment, 3 to 90 minutes in another embodiment, 5 to 50 minutes in another embodiment. In the event that the conductive paste is heat-curable, the applied paste can get cured by evaporations of solvent and/or by the molecular structure in the thermosetting polymer turned into net-like structure under the heat.

In another embodiment, the conductive paste can be heated at 50 to 120° C. just to be non-viscous before the pressing step (C). The electrode can be heated again after the pressing step (C) at relatively high temperature, for example 100 to 350° C., to be firmly cured. In the event of heating the electrode twice, the method of manufacturing a non-firing type electrode comprising steps of: (A) applying a conductive paste on a substrate; (B) heating the applied conductive paste at 50 to 120° C. to form an electrode; (C) pressing the electrode at 10 to 1000 kN/m² of plane surface pressure or at 5 to 300 kN/m of linear pressure; and (D) heating the pressed electrode at 100 to 350° C., in an embodiment. The heating temperature in the heating step (D) can be 110 to 220° C. in another embodiment, 120 to 180° C. in another embodiment.

A heating machine such as an oven, a dryer, and a furnace that can control the temperature can be used for heating.

The electrode can be obtained by heating the applied conductive paste. The applied conductive paste which is non-viscous by being heated to have electrical conduction is called "electrode" in this specification.

In an embodiment, the electrode is pressed at 5 to 300 kN/m of linear pressure in the direction of P1 by a roll **12** moving on the upper surface of the electrode **101** in the direction of D1 as illustrated in FIG. 1B and FIG. 1C.

The linear pressure is a pressure on line on the upper and/or rear surface of the electrode. The linear pressure moves to one direction to press entire upper surface and/or rear surface of the electrode.

The pressure strength can be selected according to, for example, thickness of the electrode, kind of the conductive powder, or type of the substrate. The linear pressure can be 22 to 200 kN/m in another embodiment, 35 to 125 kN/m in another embodiment, and 45 to 98 kN/m in still another embodiment. By being pressed in such range, resistivity of the electrode can be lowered as shown in Example below.

In the event of employing the liner pressure, the substrate 21 on which the electrode is formed can be a continuous roll 22 and pressed with the calendar roll 20 in a roll to roll system in another embodiment as illustrated in FIG. 2. The substrate can be a polymer film which is flexible enough to make the roll 22 when employing the roll to roll system. The substrate 21 is threaded through the calendar roll 20 which linearly presses the electrode on the substrate. "Calendar" is in general a machine having two or more rolls to thread a substance between the rolls to press the substance.

The electrode 101 can be also pressed at 10 to 1000 kN/m² of plane surface pressure. The plane surface pressure is a pressure on the entire upper and/or rear surface of the electrode 101 at the same time. Any method to make the plane surface pressure can be available, for example crank press, crankless press, or knuckle joint press. Presumptively air bobble between the conductive particles in the electrode could be pushed out of the electrode by the press to result in getting high conductivity.

The surface pressure can be 32 to 720 kN/m² in another embodiment, 65 to 580 kN/m² in another embodiment, and 100 to 470 kN/m² in still another embodiment.

The pressing is carried out just once or twice in an embodiment. The electrode could obtain lower resistivity by pressing just once as shown in Example below. Being pressed three times or more could damage the electrode and the substrate.

The method of manufacturing the electrode can optionally employ photolithography. In the event of photolithographic method, the conductive paste is photosensitive and the method can further contain a step of exposing the electrode to light to cure between the step of heating (B) and the step of pressing (C) or after the step of pressing (C). In another embodiment, the method of manufacturing the non-firing type electrode comprises steps of (A) applying on a substrate a conductive paste, (B) heating the applied conductive paste to form an electrode, (E) exposing the electrode to light, and (C) pressing the electrode. In another embodiment, the method of manufacturing the non-firing type electrode comprises steps of (A) applying on a substrate a conductive paste, (B) heating the applied conductive paste to form an electrode, (C) pressing the electrode, (E) exposing the electrode to light.

The exposing condition can be controlled according to photosensitivity of the photosensitive paste and thickness of the applied conductive paste. The cumulative exposure is 50 to 2000 mJ/cm² in an embodiment.

When the conductive paste or the substrate is unfavorable to be wet, the electrode is formed by applying the conductive paste with a desired pattern and exposed to light without an aqueous development.

However when both of the substrate and the electrode are fine to be wet, the exposing step can be followed by a developing step with an aqueous solution. The photolithographic method using the developing step is advantageous especially when forming a fine pattern. The fine pattern can comprises lines with width of 1 to 200 μ m and space between the lines of 1 to 200 μ m in an embodiment; width of 5 to 160 μ m and space between the lines of 3 to 160 μ m in another embodiment; width of 10 to 110 μ m and space between the lines of 3 to 110 μ m in another embodiment. The thickness of the fine pattern electrode can be 1 to 20 μ m in an embodiment.

The aqueous solution can be an alkaline solution such as a 0.4% sodium carbonate solution. The aqueous solution can be sprayed to the exposed conductive paste to remove the unexposed area of the conductive paste so that the cured pattern by the photo-energy shows up.

For the photolithographic method and photosensitive conductive paste, U.S. Pat. Nos. 5,143,819, 5,075,192, 5,032,490, 7,655,864 can be herein incorporated by reference.

The method of manufacturing the non-firing type electrode can be applicable to any electrical devices. In an embodiment, the electrical devices such as solar cell, resistor, capacitor, heater, touch panel, sensor, membrane touch switch, and defogger on an automotive window can contain the non-firing type electrode manufactured by the method explained above.

Conductive Paste

The conductive paste used in the method can be any type such as heat-curable and photosensitive. The conductive paste comprises at least (i) a conductive powder and (ii) an organic vehicle. The conductive paste materials are explained in detail below.

(i) Conductive Powder

The conductive powder is a powder made of any material having electrical conductivity.

The conductive powder comprises conductive material selected from the group consisting of aluminum (Al), nickel (Ni), copper (Cu), silver (Ag), gold (Au), platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), molybdenum (Mo), tungsten (W), carbon black, graphite, tin (Sn), bismuth (Bi), lead (Pb), indium (In), gallium (Ga), and a mixture thereof in an embodiment. The conductive powder comprises conductive material selected from the group consisting of, copper (Cu): silver (Ag), tin (Sn), bismuth (Bi), alloy thereof and a mixture thereof in another embodiment. An alloy of the metals can be used in the conductive powder in another embodiment. Such conductive materials can be relatively easily obtainable in the market.

The conductive powder is 100 parts by weight in an embodiment.

The conductive powder can be in any shape such as spherical, flaky, or nodular. A mixture of one or more of spherical powder, flaky powder, or nodular powder can be also available. Especially for the non-firing type electrode, the conductive powder comprises flaky conductive powder in an embodiment. The flaky powder could render larger conductivity to the formed electrode by contacting each other with larger area than spherical powder in the electrode. In an embodiment, the conductive powder comprises 80 to 100 wt % of flaky conductive powder based on the weight of the conductive powder.

There is no restriction on the particle size of the conductive powder. The particle diameter (D50) can be 0.1 to 50 μ m in an embodiment, 1 to 35 μ m in another embodiment, 1.5 to 10 μ m in another embodiment. The particle diameter (D50) corresponds to 50% of the integrated value of the number of particles when the particle size distribution is prepared. The particle size distribution can be prepared using a commercially available measuring device such as the X100 by Microtrac.

(ii) Organic Vehicle

The conductive powder is dispersed into the organic vehicle to form a viscous composition called "paste", having suitable viscosity for applying on a substrate with a desired pattern.

There is no restriction on the composition of the organic vehicle. The organic vehicle can comprise at least an organic polymer and optionally a solvent in an embodiment.

A wide variety of inert viscous materials can be used as the organic polymer. The organic polymer can comprise thermosetting resin, thermoplastic resin, or a mixture thereof.

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The thermosetting resin can be epoxy resin, melamine resin, urea resin, unsaturated polyester resin, alkyd resin, polyurethane resin, an organic-inorganic hybrid resin or a mixture thereof.

The thermoplastic resin can be phenol resin, polyethylene, polypropylene, polyethylene terephthalate, polyamide, polyamide-imide, acrylic resin, phenoxy resin, cellulose resin or a mixture thereof.

The organic polymer comprises a mixture of the thermosetting resin and the thermoplastic resin, such as a mixture of epoxy resin and phenoxy resin.

The organic polymer can be 1 to 10 parts by weight in an embodiment, 1.5 to 7 parts by weight in another embodiment.

In the event of the photosensitive conductive paste, the organic vehicle further comprises a photopolymerization initiator and a photopolymerizable compound. The conductive paste that contains the organic vehicle including the photopolymerization initiator and a photo-polymerizable compound can be cured by being exposed to light in the photographic method.

The photo-polymerization initiator is a compound that generates a free radical when it is exposed to an actinic ray. The photo-polymerization initiator can be, for example ethyl 4-dimethyl aminobenzoate (EDAB), diethylthioxanthone (DETX), and 2-Methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one. The photo-polymerization initiator can be 0.1 to 3 parts by weight in an embodiment.

The photo-polymerization compound can comprise an organic monomer or an oligomer that includes ethylenic unsaturated compounds having at least one polymerizable ethylene group. Examples of the photo-polymerization compound are ethocylated (6) trimethylolpropane triacrylate, and dipentaerythritol pentaacrylate. The photo-polymerization compound can be 3 to 10 parts by weight in an embodiment.

In the event of the photosensitive conductive paste, the organic polymer can comprise acrylic polymer having a side chain of a hydroxyl group or a carboxyl group, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl hydroxypropyl cellulose or a mixture thereof. Such polymer can be soluble in the aqueous solution such as 0.4% sodium carbonate solution in the step of developing the exposed paste.

For the photosensitive conductive paste, U.S. Pat. Nos. 5,143,819, 5,075,192, 5,032,490, 7,655,864 can be herein incorporated by reference.

The solvent such as dibasic ester, texanol and terpineol can be used to adjust the viscosity of the conductive paste to be preferable for applying onto the substrate. The solvent can be 5 to 35 parts by weight in an embodiment.

The organic vehicle can be, to 100 parts by weight of conductive powder, 5 to 90 parts by weight in an embodiment, 7 to 61 parts by weight in another embodiment, 9 to 42 parts by weight in another embodiment.

The organic vehicle can further comprise an organic additive such as a dispersing agent, a stabilizer and a plasticizer in an embodiment.

The conductive paste can further comprise an inorganic additive such as a metal oxide or a color pigment and/or an organic additive such as a dispersant and a surfactant.

The viscosity of the conductive paste can be 5 to 300 Pascal second in an embodiment, 8 to 100 Pa·s in another embodiment. The viscosity can be measured with a viscometer Brookfield HBT using a spindle #14 at 10 rpm at room temperature.

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EXAMPLE

The present invention is illustrated by, but is not limited to, the following examples.

Example 1

The electrode was formed with the heat-curable conductive paste.

18 parts by weight of dibasic ester (DBE-9 from INVISTA Inc.) as the solvent and 2 parts by weight of phenoxy resin were mixed together at 100° C. until the resin dissolved to form the organic vehicle.

100 parts by weight of flaky Ag powder with D50 of 4 μ m was dispersed well into the organic vehicle to form the heat-curable conductive paste.

The viscosity of the conductive paste was 50 Pa·s as measured with a viscometer Brookfield HBT using a spindle #14 at 10 rpm at room temperature. The degree of the dispersion was measured by fineness of grind (FOG). A typical FOG value was adjusted to 20/10 or less.

The conductive paste was screen printed through a 250 mesh screen mask onto a PET film substrate.

The electrode was obtained by heating the applied conductive paste at 80° C. for 10 minutes. The pattern of the electrode was 50 mm square with thickness of 10 μ m.

The electrode was pressed through a hydraulic calendar roll (Yuri roll Co., Ltd.) having two rolls to press at linear pressure of 61 kN/m and roll speed of 1 m/min.

The pressed electrode was heated again at 150° C. for 30 minutes to firmly cure.

The volume resistivity of the formed electrode was measured with a resistivity meter (LORESTA-GP from Mitsubishi Chemical Co., Ltd.) before the calendar press and after the calendar press.

Example 2

The electrode was formed and the volume resistivity was measured in the same manner with Example 1 except for using spherical Sn powder with D50 of 8 μ m (AT-Sn No. 600, Yamaishi Metal Co., Ltd.) instead of Ag powder in the conductive paste.

Example 3

The electrode was formed and the volume resistivity was measured in the same manner with Example 1 except for using flaky Cu powder with D50 of 3.2 μ m (1200YP, Mitsui mining & smelting CO., Ltd.) instead of Ag powder in the conductive paste.

Example 4

The electrode was formed with the photosensitive conductive paste.

The process was carried out under yellow light. Precautions were taken to avoid dirt contamination, as contamination by dirt during the preparation of the paste and the manufacture of the parts would have resulted in defects.

11 parts by weight of texanol as the solvent and 3.5 parts by weight of a mixture of acrylic polymer and hydroxypropyl cellulose as the organic polymer were mixed together at 100° C. until all the organic polymer had dissolved. 0.7 parts by weight of the photopolymerization initiator and 0.5 parts by weight of the stabilizer were added to the mixture and stirred at 75° C. The mixture was filtered through a twenty micron

filter. 5.6 parts by weight of the photolymerizable monomer was added to the filtered mixture and further mixed well to form the organic vehicle.

100 parts by weight of the flaky Ag powder having D50 of 2 μm was dispersed well into the organic vehicle to form the photosensitive conductive paste. The viscosity of the conductive paste was 10 Pa·s as measured with a viscometer Brookfield HBT using a spindle #14 at 10 rpm at room temperature. The degree of the dispersion was measured by fineness of grind (FOG). A typical FOG value was adjusted to 10/5 or less.

The conductive paste was screen printed through a 250 mesh screen mask onto a PET film substrate. The electrode was obtained by heating the applied photosensitive paste at 80° C. for 10 minutes.

The electrode was exposed to UV light of 365 nm wave length by using a collimated UV radiation source (exposure: 300 mJ/cm²) through a photo-mask. The photo-mask had line patterns having width of 100 μm and 20 mm long. The exposed electrode was placed on a conveyor going in a spray developing device filled with 0.4% sodium carbonate aqueous solution. The electrode after developing was 100 μm wide, 20 mm long and 4 μm thick.

The electrode was pressed in the same manner in Example 1.

The electrode was heated again at 130° C. for 30 minutes in an oven.

The volume resistivity ($\Omega\cdot\text{cm}$) was measured by calculation using the following equation (1). The resistance (Ω) of the electrode was measured with a multimeter (34401A from Hewlett-Packard Company) both before calendar and after calendar. Width, thickness and length of the electrode was 0.01 cm, 0.0004 cm and 2 cm respectively in equation (1).

$$\text{Volume resistivity } (\Omega\cdot\text{cm}) = \text{Resistance } (\Omega) \times \text{width (cm) of the electrode} \times \text{thickness (cm) of the electrode} / \text{length (cm) of the electrode}$$

Result

The volume resistivity of the electrode after pressing was drastically lowered in all cases using Ag, Sn, Cu as the conductive powder (Example 1 to 4) as shown in Table 1. The electrode formed with the lithographical method also obtained lower resistivity by pressing (Example 4).

TABLE 1

Paste type		Example 1 Heat- curable	Example 2 Heat- curable	Example 3 Heat- curable	Example 4 Photosensitive
Com- position	Conductive powder	Ag 100	Sn 100	Cu 100	Ag 100
	Organic vehicle	18.6	18.6	16.9	21.2

TABLE 1-continued

Paste type		Example 1 Heat- curable	Example 2 Heat- curable	Example 3 Heat- curable	Example 4 Photosensitive
Volume Resistivity ($\Omega\cdot\text{cm}$)	Before calender	1.9×10^{-4}	5.1×10^{-3}	—*	7.6×10^{-5}
	After calender	2.4×10^{-5}	6.0×10^{-1}	1.9×10^{-3}	4.0×10^{-5}

*The volume resistivity was too high to measure.

What is claimed is:

1. A method of manufacturing a non-firing type electrode comprising steps of:

(A) applying a conductive paste on a substrate, wherein the substrate is a glass substrate, a polymer film or a ceramic substrate;

(B) heating the applied conductive paste at 50 to 350° C. to form an electrode; and

(C) pressing the electrode at 10 to 1000 kN/m² of plane surface pressure or at 5 to 300 kN/m of linear pressure.

2. The method of claim 1, wherein the electrode is pressed at 5 to 300 kN/m of linear pressure by a roll.

3. The method of claim 2, wherein the roll is a calendar roll and the substrate with the electrode is a continuous roll and pressed with the calendar roll in a roll to roll system.

4. The method of claim 3, wherein the substrate is a polymer film.

5. The method of claim 1, wherein the conductive paste comprises (i) 100 parts by weight of a conductive powder and (ii) 5 to 90 parts by weight of an organic vehicle.

6. The method of claim 5, wherein the conductive powder comprises conductive material selected from the group consisting of aluminum (Al), nickel (Ni), copper (Cu), silver (Ag), gold (Au), platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), molybdenum (Mo), tungsten (W), carbon black, graphite, tin (Sn), bismuth (Bi), lead (Pb), indium (In), gallium (Ga), and a mixture thereof.

7. The method of claim 5, wherein the conductive powder comprises flaky shape conductive powder.

8. The method of claim 5, wherein particle diameter of the conductive powder is 0.1 to 50 μm .

9. The method of claim 1, wherein the electrode is heated at 50 to 120° C. in the heating step (B) and the electrode is heated again at 100 to 350° C. after the pressing step (C).

10. An electrical device comprising the non-firing type electrode manufactured by the method of claim 1.

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